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Abstract: The separate complex resonant scattering amplitudes for the two inequivalent Cu sites in $YBa_2Cu_3O_{7-\delta}$ have been determined using diffraction anomalous fine structure (DAFS). The combined amplitudes $\Delta f(\mathbf{Q}, E)$ for eight specular (00ℓ) reflections were isolated from the measured intensity using the iterative dispersion algorithm of Pickering, *et al.*, modified to accommodate contributions to the imaginary part of the scattering amplitude from the heavy Ba and Y atoms. The individual site response functions $f''(E)$ were solved by singular value decomposition of the matrix of crystallographic coefficients and applying the inverse matrix to $\Delta f(\mathbf{Q}, E)$ at each value of energy. For comparison, a second set of coefficients was obtained by simultaneously fitting the DAFS fine structure functions $\chi(\mathbf{Q}, k)$ using the computer program FEFFIT under a set of constraints. The $\chi(\mathbf{Q}, k)$ were modeled as linear combinations of the two Cu site $\chi(k)$ functions using a kinematic structure factor model with $\mathbf{Q}$ as the independent variable and theoretical $\chi(k)$ from FEFF7 .

1 INTRODUCTION

Many technologically interesting materials share the property that one species of atom occupies two or more inequivalent sites in the unit cell. Since the function of the atoms in these sites is different, it is usually necessary to study their local environment and chemical properties independently. Diffraction anomalous fine structure (DAFS) can clearly resolve the extended fine-structure and the near-edge features in the anomalous scattering amplitude $\Delta f = f' + if''$ from inequivalent resonant atoms in a diffracting material [1, 2, 3]. In some special cases, such as in the cubic spinels, the symmetry of the crystal gives Bragg reflections that contain anomalous scattering from a single resonant site only. In general, however, site separation by pure symmetry is not possible and the resonant scattering from the inequivalent sites is isolated by combining several DAFS data sets. We have applied singular value decomposition to solve the (00ℓ) DAFS from $YBa_2Cu_3O_{7-\delta}$ for the Cu(1) and Cu(2) resonant scattering amplitudes. We describe here our analysis methods and compare the experimental results to theoretical calculations by FEFF.

2 EXPERIMENTAL DETAILS

DAFS data was collected at NSLS beamline X23A2 in the vertical scattering geometry from eight specular (00ℓ) reflections of $YBa_2Cu_3O_{7-\delta}$ at the copper K edge. The sample was a 2000Å film grown by pulsed laser ablation onto a 1cm×1cm MgO (001) substrate. The c-axis was normal to the film and the crystal was fully twinned in the a-b plane. Details of the sample preparation and experiment are described elsewhere [4]. The DAFS intensity data were solved for the complex resonant scattering amplitudes at each reflection by iterative application of the Kramers-Krönig dispersion relations [2, 4] using a parameterization of the structure factor for kinematic diffraction. This analysis method requires that the crystal have a center of symmetry parallel to the photon wavevector transfer $\mathbf{Q} = \mathbf{k_f} - \mathbf{k_i}$. The computer program KKFIT performs the iterative analysis of the energy-dependent intensity using

$$I = I_0 \left[(\cos\Phi_0 + \beta f'(\mathbf{Q}, E))^2 + (\sin\Phi_0 + \beta f''(\mathbf{Q}, E))^2 \right] A(\mathbf{Q}, E, t) L(\mathbf{Q}, E) + \Delta I \qquad (1)$$

with four energy-independent adjustable parameters. Φ_0, β, I_0 and ΔI. Φ_0 is the phase of the non-resonant structure factor $|F_0|e^{i\Phi_0}$, which is the partial sum over all but the anomalous contribution from the targeted resonant atoms, and accounts for small imaginary contributions to F_0 due to anomalous scattering from the heavy Ba and Y atoms. The coefficient β of $\Delta f(\mathbf{Q}, E)$ in Eq. (1) is $\beta = \sum_j \cos(\mathbf{Q} \cdot \mathbf{R}_j) e^{-M_j} / |F_0|$, with the sum j over just the resonant atoms in the unit cell. The variables I_0 and ΔI allow the fit to adjust for an overall scale factor and constant offset in the data and have no effect on the Fourier components or normalization of the fine-structure. The energy dependent Lorentz-polarization correction $L(\mathbf{Q}, E) = (1/E^3 \sin 2\theta)$ for σ-polarized x-rays was used and the fine structure in the thin film absorption correction for specular reflections $A(\mathbf{Q}, E, t) = (1 - e^{-2\mu t/\sin\theta})/2\mu$ was determined from the fluorescence XAFS measured at the same time as the DAFS.

3 SITE SEPARATION BY LINEAR INVERSION

The output of KKFIT for each reflection is a *weighted* scattering amplitude $\Delta f(\mathbf{Q}, E)$ which is a linear combination of the individual site amplitudes $\Delta f(E)$

$$\Delta f(\mathbf{Q}, E) = \frac{\sum_{i=1}^{n} \Delta f_i(E) \sum_{j=1}^{n_i} \cos(\mathbf{Q} \cdot \mathbf{R}_j) e^{-M_j}}{\sum_{i=1}^{n} \sum_{j=1}^{n_i} \cos(\mathbf{Q} \cdot \mathbf{R}_j) e^{-M_j}} = \sum_{i=1}^{n} W_i(\mathbf{Q}) \Delta f_i(E) \tag{2}$$

for n inequivalent sites and n_i atoms occupying the i^{th} site, where $\mathbf{R}$ are the atomic positions referenced to an arbitrary origin of coordinates in the unit cell and e^{-M} are the diffraction Debye-Waller factors formally included into the structure factor sum [5].

The Fourier components of the resonance fine-structure and the position of the absorption edge are strongly dependent on the angle between the photon polarization vector and the near-neighbor bonds. In DAFS experiments there is an additional complication not present in XAFS that the incident and outgoing photons may have different polarization directions. This is an important consideration for the general n-site inversion problem where one wants to make simple linear combinations of the $\Delta f(\mathbf{Q}, E)$, since the individual site functions must be the same for all of the reflections used in the inversion. The complete energy- and polarization-dependent anomalous scattering amplitude for arbitrary orientation of $\hat{\mathbf{e}}$ and $\hat{\mathbf{e}}'$ is a tensor. In the absence of scattering that rotates the polarization, maintaining $\hat{\mathbf{e}} = \hat{\mathbf{e}}'$ is sufficient to insure that the $\Delta f(E)$ are scalar functions of energy. We fixed the polarization condition in our experiment by keeping the rotation axis of the crystal parallel to the incident photon polarization in the vertical scattering geometry during all of the DAFS scans. Since the $YBa_2Cu_3O_{7-\delta}$ film was fully twinned in the a-b plane, the resulting fine structure in $f''(E)$ is equivalent to a-b polarized XAFS.

Under these experimental conditions, measurement of the DAFS at m Bragg reflections produces a system of linear equations of dimension $m \times n$ with elements $W_i(\mathbf{Q})$. The individual site amplitudes are isolated by determining the inverse matrix W^{-1} and applying it to the set of $\Delta f(\mathbf{Q}, E)$. For the two-site problem of $YBa_2Cu_3O_{7-\delta}$ the equation to be solved is

$$\begin{pmatrix} \Delta f(\mathbf{Q}_1, E) \\ \ddots \\ \Delta f(\mathbf{Q}_m, E) \end{pmatrix} = \begin{pmatrix} W_1(\mathbf{Q}_1) & W_2(\mathbf{Q}_1) \\ \ddots & \\ W_1(\mathbf{Q}_m) & W_2(\mathbf{Q}_m) \end{pmatrix} \begin{pmatrix} \Delta f_1(E) \\ \Delta f_2(E) \end{pmatrix}. \tag{3}$$

In general, Eq. (3) will be overdetermined since the number of available reflections exceeds the number of inequivalent sites and inversion requires a singular value decomposition (SVD) or similar method to accommodate degeneracies. Figure 1(a) shows $f''(E)$ in the near-edge region for Cu(1) and Cu(2) sites obtained by SVD on the 2×8 matrix made up of the coefficients in the first two columns of Table 1. Figure 1(b) shows the individual site functions added together according to the stoichiometry of the unit cell overplotted with the fluorescence XAFS.

The coefficients $W_i(\mathbf{Q})$ can be calculated using the average atomic positions determined by crystallography, or they can be refined from the DAFS fine-structure $\chi(\mathbf{Q}, E)$ by modelling the extended fine structure as a linear combination of two fine-structure functions combined according to a kinematic structure factor model. The $W_i(\mathbf{Q})$ for eight specular reflections of $YBa_2Cu_3O_{7-\delta}$ are shown in Table 1. The values listed in the first two columns were calculated using positions refined from (00ℓ) intensities measured with a rotating Cu anode. The values in the second two columns were obtained by a constrained fit to the extended DAFS data for four reflections simultaneously using FEFFIT [7] with 25 scattering paths from FEFF7 . This approach produces a set of coefficients that are consistent with the data over the entire energy range. The FEFFIT fit was performed over the first shell only. Since the DAFS weighting can weaken the first shell signal, we were only able to co-refine these four reflections. Typical FEFFIT fits, illustrated by the (001) and (004) R-space transforms $\chi(\mathbf{Q}, R)$, are shown in Figures 1(c) and (d).

Table 1: Coefficients $W_i(\mathbf{Q})$ for the two Cu sites in $YBa_2Cu_3O_{7-\delta}$. Since the Cu(2) sitessits at roughly at $\pm\frac{1}{3}$c, the ratio of $W_1(\mathbf{Q})/W_2(\mathbf{Q})$ takes on only three distinct values as ℓ is varied in the specular reflections. Uncertainties in the FEFFIT weights are $\sim 3\%$ of the value.

	diffraction		FEFFIT	
$(hk\ell)$	$W_1(\mathbf{Q})$	$W_2(\mathbf{Q})$	$W_1(\mathbf{Q})$	$W_2(\mathbf{Q})$
(001)	-4.144	5.144	-4.112	5.112
(002)	1.858	-0.858	—	—
(003)	0.355	0.646	0.351	0.649
(004)	-1.246	2.246	-1.180	2.108
(005)	0.709	0.291	—	—
(007)	-0.951	1.951	-0.827	1.827
(009)	0.650	0.350	—	—
(0011)	0.347	0.653	—	—

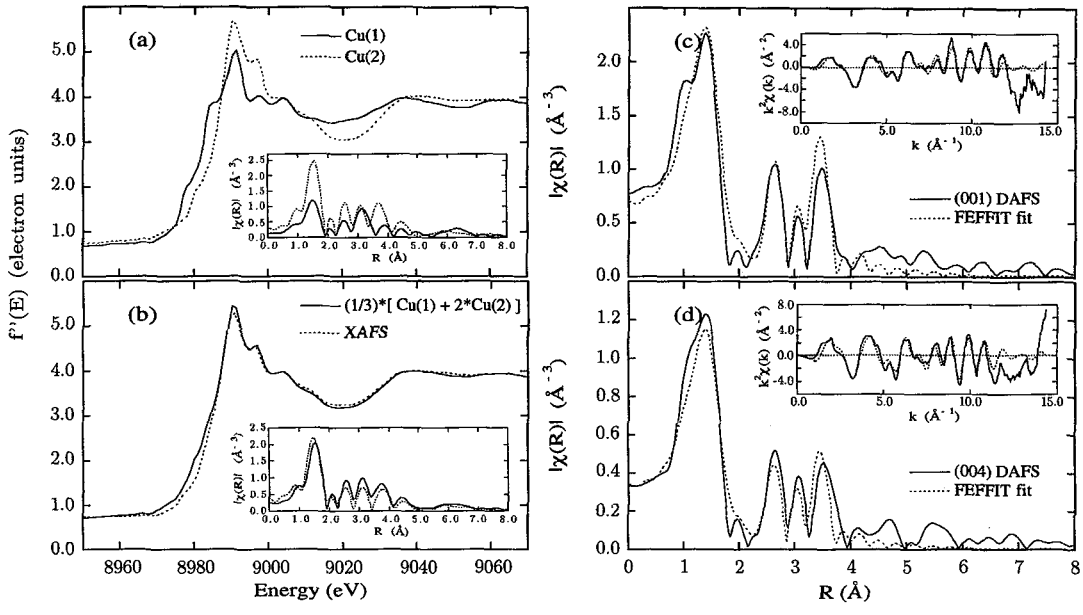

Figure 1: Overplots of the imaginary part of the Cu(1) and Cu(2) anomalous scattering amplitudes from $YBa_2Cu_3O_{7-\delta}$ DAFS data. (a) shows the site-separated $f''(E)$ (b) compares the sum of the DAFS results with the fluorescence XAFS. Insets show the R-space transforms of the corresponding $\chi(k)$ data. The figures on the right show typical FEFFIT R-space fits using FEFF7 $\chi(k)$ for 25 scattering paths. (c) (001) and (d) (004). Insets show the DAFS $\chi(\mathbf{Q},k)$ data (solid lines) and FEFFIT k-space fits (dashed lines).

4 CONCLUSION

The DAFS experiments described here were confined to a line in reciprocal space, but the analysis methods we have described can be readily extended to the full three-dimensional DAFS problem since the full tensor symmetry of the fine structure in the anomalous scattering amplitude in can be calculated using FEFF7 . In the application of FEFFIT to DAFS, we have simultaneously fit the fine structure from the entire data set subject to constraints based on the average atomic positions. This suggests the possibility of self-consistently co-refining the long-range structural parameters for the sublattice of resonant sites from the Bragg peak fine-structure. However, the normalization denominator of Eq. (2) makes the Kramers-Krönig isolated fine structure sensitive only to the difference between the diffraction Debye Waller factors for the inequivalent sites. True co-refinement of long-range and short-range structural parameters will need to model both the fine-structure and the overall peak intensities.

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